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Thermodynamic properties of pyruvic acid and its methyl ester

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ABSTRACT

In present work, a complete study of thermodynamic properties of pyruvic acid and methyl pyruvate in the condensed and gaseous phases was carried out using experimental and theoretical approaches. Enthalpies of combustion and formation of compounds were evaluated using combustion calorimetry. The transpiration method was used to determine the temperature dependence of the vapor pressures of acid and its methyl ester for the vaporization enthalpy calculation. With *ab initio* calculation it has been determined, that in gas phase pyruvic acid exists predominantly in monomeric form. The values of the enthalpy characteristics of the substances obtained using the composite method G4 were checked for reliability. A good agreement between the calculated and experimental values of the enthalpies of formation of the acid and its methyl ester in the gaseous phase is observed. The methods of quantum chemistry and statistical physics were used to calculate thermodynamic functions of compounds in the ideal gas state in temperature range 298.15–1500 K.

1. Introduction

The pyruvic acid (2-oxopropanoic acid) belongs to the class of ketoacids. The acid being a product of the glycolysis – the breakdown process of glucose in the living organism, its esters and salts contribute to the chemical activity in the cells [1]. The pyruvic acid derived from carbohydrates, fatty acids from lipids, and aminoacids from proteins is eventually converted into the compound acetyl coenzyme A in the matrix of the mitochondrion. This compound, in turn, undergoes a series of chemical reactions to generate energy through the oxidation of acetyl coenzyme A (acetyl-CoA) called the citric acid cycle, or Krebs cycle [2].

In this work enthalpies of formation in the condensed phase and enthalpies of vaporization for pyruvic acid and methyl pyruvate were determined using combustion calorimetry and transpiration technique. Results from combustion calorimetry together with the vaporization enthalpies have been used for calculation of the gas-phase standard enthalpy of formation of acid and ester at 298.15 K. In addition, we use the G4 method to calculate the molar enthalpies of compounds in the gas phase. Thermodynamic functions of the compounds in the gaseous state were computed in the range of T = 298.15–1500 K.

2. Materials and methods

2.1. Materials

Commercial samples of pyruvic acid (Acros, extra pure, 98.0%, CAS 127-17-3) and methyl ester of pyruvic acid (Alfa Aesar, 98%, CAS 600-22-6) were additionally purified by fractional vacuum distillation. No impurities (greater than 0.001 mass fractions) were detected in samples used for the thermochemical measurements (see Table S1). The degree of purity was determined using a GC equipped with an HP-1 capillary column (length of 10 m, an inside diameter of 0.53 mm, and a film thickness of 2.65 μm). The standard temperature program of the GC was T = 363 K for 120 s followed by a heating rate of 0.167 K·s^{-1} to T = 443 K. Water mass fraction in the samples was determined using a Mettler Toledo DL38 Karl Fischer titrator using the HYDRANAL™ as the reagent. A mass fraction of water in purified samples was measured by the Karl Fisher titration (352.0 and 730.7 ppm for acid and ester correspondingly) and the appropriate corrections were applied for combustion experiments.

2.2. Combustion calorimetry

The combustion energy of compounds was measured in a modified

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